New materials for hot electron generation: general discussion

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Abstract

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This article is part of the themed collection: Hot-electron science and microscopic processes in plasmonics and catalysis

Naomi Halas opened a general discussion of the paper by Alexandra Boltasseva: I am very happy that Alexandra has led the way in addressing the need for sustainable plasmonic materials. This is particularly relevant in the photocatalysis field since we have a limited supply of Pt and Pd on this planet.

Alexandra Boltasseva answered: The comment is highly appreciated. Our efforts have been simply to expand the existing material database for plasmon-driven hot electron generation so as to provide the community with more choices for specialized applications.

Zachary Schultz noted: Incorporating new materials into your devices should enable new chemical reactions to be investigated. Can you comment on any new reactions you have studied or insights your devices are providing into other possible reactions?

Alexandra Boltasseva responded: These devices can also be used for different photoelectrochemical reactions such as degradation of organic pollutants, alcohol oxidation, and some heterogeneous chemical reactions involving organic molecules. Also, the use of emerging plasmonic materials such as titanium nitride, zirconium nitride and MXenes such as titanium carbide offer the possibility to explore photocatalysis over a wide wavelength spectrum for various applications.

Bart de Nijs enquired: In your experiments you use nanodiscs on a metal film with a thin insulator spacer; these provide a very high confinement perpendicular to the surface but very little lateral confinement. For example, using spheres instead of discs will provide strong field confinements in all directions resulting in a much higher field but a smaller hotspot. Would your system benefit from lateral confinement as well or is the perpendicular confinement sufficient?

Alexandra Boltasseva replied: Any form of confinement of the electromagnetic field would in general benefit photocatalysis. For lateral confinement, the semiconductor needs to be along the sidewalls of the nanodisk as well, so as to facilitate photocatalysis. Such a design, although difficult to fabricate, would also increase water splitting efficiency. See, for example, work from Gao et al.1

1 H. Gao, C. Liu, H. E. Jeong and P. Yang, ACS Nano, 2012, 6, 234-240.

Bartlomiej Jankiewicz asked: Are there any specific reasons for using hematite instead of TiO2? Are there any advantages of hematite compared to titanium dioxide? The reasons for using hematite that you have mentioned in your article and presentation apply also to TiO2.

Alexandra Boltasseva responded: Yes, there is indeed a lot of work on hot electron generation for water splitting in TiO2. We chose hematite as it has a bandgap in the visible and therefore can provide a larger photocurrent.

Niclas Sven Mueller remarked: My question concerns the choice of plasmonic material in your study. For the gold nanostructures you presented pronounced plasmonic resonances that are spectrally well below the band gap of hematite. To my understanding this will lead to no considerable increase in the photon conversion efficiency when you integrate over the entire spectrum. Did you consider using silver instead of gold? I would not expect that oxidation at the Ag/hematite interface will be an issue as you can directly deposit silver on top of the hematite film by e-beam lithography.

Alexandra Boltasseva answered: Yes, the fact that we used gold nanodisks that gave resonances below the hematite bandgap leads to a lower photocurrent. We did investigate the possibility of using plasmonic structures that would enable us to push the resonance above the bandgap and reap the benefits of high field confinement. However, we did not use silver as it would oxidise when used in a photo-electrochemical cell.

Jeremy Baumberg asked: I am trying to understand how your water splitting works at the nanoscale details. Hole transport is a few nm, but your hematite is trapped inside the narrow gap. Where is the hydrogen being produced and how do reactants and products get in or out? Is the hematite porous or completely solid as in your TEMs? Can water get in? More generally the optical field is concentrated in inaccessible parts of the hematite so is this only a fringing field effect? If so, can we do better with a different geometry and what would this be?

Alexandra Boltasseva clarified: In our photoelectrochemical system, we used a three-electrode cell where O2 is evolved at the hematite/Au photoanode, while H2 is produced at the Pt counterlectrode. The third electrode is the reference electrode. The reactant is water, which is split to give H2 and O2 (the products), that could be separated by gas membrane technology in a real system.

Hematite is completely solid as shown by TEM images reported in the manuscript. Water cannot get inside the solid. The optical fields are concentrated in the inaccessible parts of the hematite. So the measured photocurrent enhancement is only due to those hot carriers, generated from plasmon decay, that contribute to the surface chemical reaction (oxidation of water).

We do believe that the fact that hematite is sandwiched between the gold mirror and gold nanodisks hinders the hot electron injection. We are currently working on a different geometry that would enhance hot electron injection into the semiconductor and hope that we can report our results in the near future.

Madasamy Thangamuthu enquired: A constant voltage of 1.5 V is applied for photocurrent measurement; is there any reason behind this value? The literature uses different numbers – I don't understand why and how I can choose the right potential. Is it to offset the electrical double layer potential formed at the electrode–electrolyte interface?

Alexandra Boltasseva replied: Chronoamperometry measurements can be done at any potential and the choice is somewhat arbitrary. However, the potential is usually chosen such that it corresponds to the generation of a plateau photocurrent in the J–V curve. Depending on the shape of the J–V curve one can choose different potentials which would provide photocurrents representing the photoanode performance working in different regimes.

Hongxing Xu queried: Which structure is ideal for photoelectron generation? Is a rough surface or a sharp edge good?

Alexandra Boltasseva replied: I am not sure what exactly is the difference between rough surfaces and sharp edges. In general, strong electromagnetic fields at the surface can lead to an enhanced photoelectric effect from the metal surface. There are many articles in the literature which discuss the role of geometry and surfaces on photoelectron generation. For example, ref. 1.

1 A. M. Brown, R. Sundararaman, P. Narang, W. A. Goddard III and H. A. Atwater, ACS Nano, 2016, 10, 957–966.

Jacob Khurgin commented: It is important that the efficiency of any process involving photo (plasmon) generated hot carriers depends on two factors:

(A) Absorption efficiency – i.e. what percentage of the incoming line is absorbed;

(B) Emission efficiency – i.e. what percentage of carriers generated by absorbing photons (directly or via plasmons) actually come out and do useful work.

It seems to me that often we are concerned with the first and in my view it is not all that important as in the end, once you have enough catalyst such as TiO2 a significant portion of light will be absorbed anyway and there is no shortage of titanium. Whether it is 80% or 100% makes a very small difference in the overall efficiency given that efficiency (B) is measured in a fraction of a percent. Therefore, we should use plasmons judiciously, for example if we could extend the absorption edge into longer wavelength regions. Making fancy structures just because we can only redistributes absorption but it also introduces additional loss in the metal.

Giulia Tagliabue asked: Do you have any estimate of the Schottky barrier between gold and hematite? I would expect that depending on this parameter and the photon energy, a fraction of the hot-holes generated in gold could be transferred to the p-type hematite. Do you have any estimate for this process and what would be its contribution in the visible regime versus the infrared regime?

Alexandra Boltasseva responded: By using the Mott-Schottky rule (work function of Au = 5.1 eV; electron affinity of hematite = 4.85 eV; see work by Hankin et al.1) we estimate a Schottky barrier height of 0.25 eV. This value tells us that by using this diode configuration we might also collect NIR hot carriers. In this system, hematite in an n-type semiconductor and under photoelectrochemical conditions holes migrate toward the electrolyte while electrons move into the external circuit. Therefore, hot holes generated in plasmonic Au nanodisks travel toward the electrolyte and may directly react with water (i.e. the catalytic effect of the plasmonic metal) to oxidize it.

1 A. Hankin, J. C. Alexander and G. H. Kelsall, Phys. Chem. Chem. Phys., 2014, 16, 16176–16186.

Sylwester Gawinkowski remarked: You have shown that the electromagnetic properties of ceramic materials can be changed by changing their composition and they can mimic the plasmonic properties of metals. The compositions of such ceramic materials are fundamentally limited by the limited number of elements in the periodic table. Is there any other fundamental limit and how similar can such ceramic materials be to perfect metals?

Alexandra Boltasseva answered: The optical properties of ceramic materials will of course depend on the composition chosen. For example while titanium nitride and zirconium nitride are highly metallic (carrier concentration ~1022 cm-3), other nitrides like tantalum and hafnium nitride do not have such high carrier concentration. Eventually it boils down to how the atomic arrangement in the lattice provides a high enough density of states at the Fermi level with relatively high mobility to get good plasmonic metal-like behavior.

Jeremy Baumberg opened a general discussion of the paper by Mahfujur Rahaman: There is another explanation for your TERS rings, which I believe is more likely. You have strong excitons in the monolayer TMD, which are oriented in-plane (you can see many papers reporting this). In your plasmonic tip-disk geometry, the field orientation is normally perpendicular to the disk so does not couple to these excitons. However, at the disk edges there is an increasing in-plane component which couples to the excitons. Although your SERS laser is at a longer wavelength, there is still a very strong SERS enhancement from the resonant electronic states of the exciton (again extensive literature exists, for instance on spin-flip Raman in semiconductors in the 1980s-90s). Hence you are seeing TERRS (tip-enhanced resonant Raman scattering) which in this geometry appears as rings where there is an in-plane field. One way to check would be to look at hBN which has no exciton. Have you tried this?

Mahfujur Rahaman replied: Many thanks for your suggestion. However, we disagree that in plane excitons are a more likely cause of our TERS enhancement. We used an excitation laser of 785 nm (1.58 eV) which is much below the optical band gap (1.9 eV) of monolayer MoS2. Therefore, if there is an excitonic contribution due to the reason you mentioned that would not be that significant. Typical as measured TERS spectra taken at the edge of the Au disk and on Si are shown here in Fig. 1. As one can see, at the edge the TERS signal of monolayer MoS2 is much stronger resulting in the TERS images we have presented in our work. Additionally, if there was any excitonic effect then one would also expect an increased background which is clearly missing in the spectra.

Fig. 1 Typical as measured TERS spectra taken at the edge of the Au disk and on Si.

Javier Aizpurua commented: When interpreting the TERS signal in terms of local fields, your paper shows a description based on a modelling of sharp edges of the structures. How realistic are these sharp edges that you modeled? Figure 2(c) in your paper shows a very symmetric image profile around the disks. Wouldn't one expect more directional enhancement, following the polarization of the incident light? Why do you not have a more asymmetric field enhancement? In that TERS image, the intense signal spreads over almost 50 nm – but that is not what you get from the ultrasharp edges. Is there a certain roughness that might spread the signal and explain the contrast?

Mahfujur Rahaman responded: In our TERS image we have observed a ring-like shape following the rim of the Au disks as is shown in Fig. 2 in our paper. In the experiments the shape of the TERS images were systematic and reproducible. To understand the TERS images we introduced an FEM simulation in which we modelled a Au disk of similar dimensions to those used in the experiment. We also excited the disk in the same experimental configuration. The simulated TERS image shows a ring-like shape along the edges of the disk. However, you are right that in the simulation the edge of the Au disk was sharp resulting in a very narrow width of the TERS distribution. In reality, the edge of the Au disks may not be that sharp and therefore the electric field distribution may not be identical. Hence there is a deviation from the experimental situation to the theoretical model. However, the purpose of the simulation is to understand the TERS behaviour (which causes the ring-like shape), which the simulation successfully explained. The angle of incidence of the excitation and collection was 65°. This angle was chosen in order to maximize the direction of the excitation electric field

parallel to the tip long axis. In this configuration the ratio between the out-of-plane and in-plane components of the electric field is 2.14. Also, one shall expect TERS enhancement due to the out-of-plane component if we only consider the tip. However, the in-plane component will introduce a slight asymmetry in the ring shape on the Au disk which we also observe in the simulation, though in the experimental images the asymmetric pattern was hardly observed. This may be because of the weak contribution of the in-plane component. You are right that in the high resolution experimental TERS images we observed a more broad distribution. This may be because of the roughness of the Au surface on top of the disk as you mentioned. Moreover, the experiment was performed when the tip was in contact with the MoS2 film meaning a slight deformation of the film was also expected which could also change the interaction between the tip and the Au disk.

Zachary Schultz continued the discussion: In your response to Javier, you commented that the tip deforms the MoS2 overlayer. Can you comment on the force provided by the tip? From your schematic, the MoS2 layer should be further from the gold structures in the middle and touch near the edges. Is the deformation force enough to push the MoS2 onto the Au pillars to maintain a uniform distance between the tip, MoS2, and gold structures underneath?

Mahfujur Rahaman answered: The TERS spectra were acquired when the tip was in contact with the MoS2 film. This is a special mode designed in the HORIBA NanoRaman platform to maximize the TERS signal. In general the AFM system is operating in intermittent contact mode meaning a soft contact with the sample. Now in the TERS configuration the system permits you to hold the tip onto the probe surface for the accusation time period and this repeats in every oscillation cycle of the tip. Therefore, the amount of the force acting on the film by the tip is minimal and you can control that by changing the tip–sample distance. However, in the default condition optimized by the system, the exerting force is in the range of a few nN. However, for this current experiment we did not measure the exact value.

Thanks to the very good flexibility of the MoS2 film and also the very good affinity to Au, the MoS2 film nicely follows the morphology of the Au nanostructures. This is also confirmed by our AFM and SEM images of the sample (please see our previous work1,2). Unless there is any twisting or wrinkle, MoS2 has a homogeneous coverage. However, you are right that the slight force exerted by the tip can also help to keep the tip–sample distance uniform.

1 M. Rahaman, R. D. Rodriguez, G. Plechinger, S. Moras, C. Schüller, T. Korn, and D. R. T. Zahn, Nano Lett., 2017, 17, 6027–6033.

2 A. G. Milekhin, M. Rahaman, E. E. Rodyakina, A. V. Latyshev, V. M. Dzhaganc and D. R. T. Zahn, Nanoscale, 2018, 10, 2755–2763.

Sebastian Schlücker remarked: In UHV-TERS on molecules, colleagues from Hefei in China have reported sub-nm spatial resolution which equals intramolecular resolution. What is the best spatial resolution known for TERS on semiconductor samples?

Mahfujur Rahaman replied: For organic molecules the reported spatial resolution is about 0.5 nm.1 For semiconducting CNTs the reported spatial resolution is about 0.7 nm.2 For 2D semiconductors we have achieved a spatial resolution of 2.3 nm.3

1 R. Zhang, Y. Zhang, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang and J. G. Hou, Nature, 2013, 498, 82–86.

2 M. Liao, S. Jiang, C. Hu, R. Zhang, Y. Kuang, J. Zhu, Y. Zhang and Z. Dong, Nano Lett., 2016, 16, 4040–4046.

3 A. G. Milekhin, M. Rahaman, E. E. Rodyakina, A. V. Latyshev, V. M. Dzhaganc and D. R. T. Zahn, Nanoscale, 2018, 10, 2755–2763.

Preeti Deshpande asked: How can you decouple the effects due to strain and doping from the Raman spectra of MoS2 since both affect the peak position? Also could you give some reference works for doing this?

Mahfujur Rahaman answered: MoS2 has two well-known first order Raman modes in the form of in-plane E2g and out-of-plane A1g. Due to vibrational symmetry these two modes are sensitive to strain and doping differently. For more details you can check any strain and doping related study of MoS2. Perhaps the two articles by Lloyd et al.1 and Chakraborty et al.2 would be helpful.

In our work we have investigated the peaks to decouple strain, local temperature rise, and hot electron doping. Since the in-plane E2g mode is more sensitive to strain and non-sensitive to electron–phonon coupling via doping we focused on this particular mode for strain measurement. However, high frequency modes around 450 cm-1 are also sensitive to strain and we monitored these peaks' evolution to quantify the strain in the MoS2 system with local temperature rise. The out-of-plane A1g mode was then monitored to quantify the hot electron doping effect. For more details please check our recent papers.3,4

1 D. Lloyd, X. Liu, J. W. Christopher, L. Cantley, A. Wadehra, B. L. Kim, B. B. Goldberg, A. K. Swan, and J. S. Bunch, Nano Lett., 2016, 16, 5836–5841.

2 B. Chakraborty, A. Bera, D. V. S. Muthu, S. Bhowmick, U. V. Waghmare and A. K. Sood, Phys. Rev. B, 2012, 85, 161403(R).

3 A. G. Milekhin, M. Rahaman, E. E. Rodyakina, A. V. Latyshev, V. M. Dzhaganc and D. R. T. Zahn, Nanoscale, 2018, 10, 2755–2763.

4 M. Rahaman, R. D. Rodriguez, G. Plechinger, S. Moras, C. Schüller, T. Korn, and D. R. T. Zahn, Nano Lett., 2017, 17, 6027–6033.

Tae Kyung Lee enquired: (1) Is there an effect of the curvature of MoS2 on the TERS intensity or the generation of hot electrons?

(2) Is there a MoS2 phase transition caused by the hot electrons of the Au nanocylinder? And how does this phase transition affect the TERS intensity?

Mahfujur Rahaman responded: Since MoS2 was exfoliated on a Au nanodisk array, it created a carpet-like structure on top, which one can also see in the AFM and SEM images.1 From the topography it is clear that MoS2 follows the Au disk morphology resulting in curvature. We have quantified the strain distribution in the MoS2 curvatures using TERS. Regarding the TER intensity, what we observed is a more or less homogeneous distribution of the TERS intensity along the disk rims or edges. Using FEM simulation we explained that this enhancement is related to the plasmonic field created in the hot spots between the tip and the disk. Moreover, we also observed a strong hot electron doping in MoS2 of the order of 1013 cm-2. Due to this strong doping we observed that MoS2 underwent a phase transition from 1H to 1T. And interestingly, this phase transition was highly localized in the hot spots where we observed the strongest TERS intensity as well. The work we have presented in this article is the continuation of the work we published previously.1 All the physical phenomenon related to the MoS2 properties were discussed in that contribution. In the present contribution we have investigated the physical process of TERS enhancement and therefore no discussion regarding the properties of MoS2 is included. We would kindly request that you read our previous paper1 in which we quantified the strain, local temperature rise and plasmonic hot electron doping effects on MoS2.

1 A. G. Milekhin, M. Rahaman, E. E. Rodyakina, A. V. Latyshev, V. M. Dzhaganc and D. R. T. Zahn, Nanoscale, 2018, 10, 2755–2763.

Naomi Halas questioned: What are some of the real challenges where we could use more theoretical focus? What would it take to really advance the field?

Mahfujur Rahaman replied: Many thanks for this question. As an experimental physicist working on 2D material systems, I think one of the key areas in this field is the control of the local optical properties of 2D semiconductors, which is one of the black boxes to understand for nanoelectronic devices. Tip enhanced optical (TEO) measurements not only help us to understand local properties of the materials but can also help us to tune or modify the local properties as well. In particular, if we operate the TEO measurements in the quantum mechanical regime by reducing the tip–sample distance to a few angstrom, then for example hot electrons surely have a significant say in the local physical properties. This is very important for 2D semiconductors since they are ultra sensitive to any change in local environment. I think it is an interesting field for both experimentalists and theoreticians to work together.

Alexandra Boltasseva contributed: To really advance the field of plasmon-induced hot electrons, I feel the field should branch out to other areas of science and technology such as photostimulation in biology, spintronics and magnetic memory etc. For example a couple of reports of plasmon decay and subsequent thermal heating on neuronal action potentials can be found in the literature.1 Study of hot electron mediated localized neuronal firings can be of immediate significance to the bio-community. Similarly hot electron mediated ultrafast magnetization dynamics has also been reported in the literature.2 Studying hot electron mediated processes in magnetic materials could open up an avenue for plasmonic applications in spintronics and magnetic memory beyond HAMR. Needless to say that these explorations would demand a lot from theoreticians to take their existing knowledge of hot electron dynamics and apply it to scientific fields different from semiconductor/metal mediated photochemistry.

1 J. L. Carvalho-de-Souza, J. S. Treger, B. Dang, S. B. H. Kent, D. R. Pepperberg and F. Bezanilla, Neuron, 2015, 86, 207–217.

2 Y. Yang, R. B. Wilson, J. Gorchon, C.-H. Lambert, S. Salahuddin and J. Bokor, Sci. Adv., 2017, 3, e1603117.

Mahfujur Rahaman addressed the room: In our TERS experiments we use Au nanodisks which have an LSPR around 610 nm. The LSPR position is also confirmed by the SERS experiments. However, when we brought down the Au tip for the TERS experiments we observed the strongest enhancement for 785 nm. We know that in a dimer situation, due to the restoring force, the combined LSPR should red shift. However, in our case the red shift is quite strong. We do not have any theoretical study of the observed strong red shift of the system. If any one can help us in the understanding of this phenomenon it would be really great.

Javier Aizpurua noted: Our contribution in this Faraday Discussion is focused on the optical field emission in plasmonic gaps subjected to intense single-cycle optical pulses, however, we have studied the plasmonic response of nanoparticle dimers and gaps since many years ago. I can refer to our seminal paper on single molecule spectroscopy in gaps, where we already reported the redshift of the gap plasmon,1 or to the theoretical paper that described this effect for very narrow gaps.2

The understanding of the plasmonic redshift in a gap is clear at this point as originating from the interaction of the surface charges at both sides of the gap (either dipole–dipole interaction for a large separation, or multipole-multipole interaction for narrower gaps). If one considers the SERS and TERS signal as approximately proportional to the 4th power of the local field enhancement, the spectral shifts that you find might be consistent with the use of the very narrow gaps that you achieve in your TERS configuration (the tip–sample gap). If this separation does not fully explain the enhancement, one might need to account for other more subtle effects connected with non-locality, charge transfer mechanisms, or optomechanical effects which can produce extra enhancement of the TERS signal.

1 H. Xu, J. Aizpurua, M. Käll and P. Apell, Phys. Rev. E, 2000, 62, 4318–4324.

2 I. Romero, J. Aizpurua, G. W. Bryant and F. J. García de Abajo, Opt. Express, 2006, 14, 9988–9999.

Javier Aizpurua continued: How plasmonic spectral shifts happen due to tip-substrate interactions is clear. However, the reduction or enhancement of the Raman signal could be due to many effects which can go beyond the local field enhancement of the plasmonic antenna. One can find resonant effects, shifts between the near field and the far field. Sometimes a local field description is very good, but for others one needs to include quantum effects. Also, often one needs to include the presence of the molecule or the excitonic material and consider its electronic structure as part of the whole response and enhancement. In other words, I would like to note that accurate modelization of Raman signals from molecular species often requires going beyond electromagnetics.

Mahfujur Rahaman answered: Many thanks for the comments. When we have performed SERS on these Au disks, we observed the strongest signals for the 638 nm laser and no signal for the 785 nm laser. Therefore, our initial assumption was that we could perform TERS better using the 638 nm laser since it is in resonance with the MoS2 and also the disks. However, after conducting TERS it turned out that the 638 nm laser had little impact in TERS and the 785 nm laser had the strongest. Since we do not have a laser of higher wavelength than 785 nm we could not try this. This phenomenon surprised us a lot since the shift is quite big if we only think of LSPR of the combined system only. However, you are absolutely right in your comments that it may not only be about plasmonic enhancement. We are now investigating this issue and hopefully will be able to get an answer.

Alexander Govorov remarked: In our studies of hot electron (HE) generation, we found that size, shape and material matter. Since hot-electron generation is a quantum surface effect, small sizes of nanocrystals are preferable. The efficiency of HE generation increases strongly for nanocrystals with complex shapes and hot spots, such as nanostars, nanocubes and metamaterial absorbers with gap plasmons. Nonthermal HEs with high energies are generated due to non-conservation of linear momentum, and such processes are very efficient near surfaces and in plasmonic hot spots. Since the HE generation is a quantum process, metals with a longer mean-free path will work better. For example, silver is more efficient than gold. The quantum efficiency of HE generation also increases in

the infrared spectral interval because the quantum amplitudes of HE generation grow for small photon quanta. Detailed description for the above properties can be found in our papers.

To be more specific, the energy efficiency of creation of high-energy hot electrons in nanocrystals (NCs) with simple shapes (nanospheres and nanorods) is given by the ratio1lmfp/a, where lmfp is the mean fee path and a is the size of a nanocrystal. This simple equation for the efficiency can also be derived from the equation for the surface-induced decay rate of a plasmon in a NC.2,3 For this, we need to take a ratio between the surface-decay rate of a plasmon and the decay rate of a plasmon in the bulk. Overall, the effect of decay of plasmons due to the generation of high-energy electrons near the surfaces has a long history.2,3

1 L. V. Besteiro, X.-T. Kong, Z. Wang, G. Hartland, and A. O. Govorov, ACS Photonics, 2017, 4, 2759–2781.

2 L. Genzel, T. P. Martin and U. Kreibig, Z. Phys. B: Condens. Matter, 1975, 21, 339–346.

3 U. Kreibig and M. Vollmer, Optical Properties of Metal Clusters, Springer-Verlag Berlin Heidelberg, 1995, vol. 25.

Jacob Khurgin responded: Agreed. In my paper it is clearly stated that in the end it is the surface to volume ratio that must be maximized for maximum HE emission efficiency.

Jacob Khurgin commented: In my view the most important work for theorists is to study hybridization at the surface of the metal. There lies the key to efficiency.

Emiliano Cortes noted: I totally agree that this is one of the most interesting directions for the field, not only because of efficiency but more important to me for selectivity of the generated products. Our current knowledge of the electronic structure of adsorbed molecules is very limited, more so if we want to access the excited states.

Anatoly Zayats asked: In the case of the film on top of the disk structure probed by the tip, the excitation of the localised plasmon will lead to a strong field enhancement and may result in photoelectron injection from the gold disks to the film. This may change the observed spectra. Have you considered these effects?

Mahfujur Rahaman replied: Yes we have considered that and you are absolutely right about hot electron injection. Due to strong hot spot formation between the tip and the Au disks (which sandwiched the monolayer MoS2 in between), we observed selective doping. The doping sites were

concentrated on the hot spots only. In our previous publication1 we have reported this phenomenon. Due to strong hot electron doping, we observed a structural phase change from the semiconducting 1H to the metallic 1T phase. Thanks to our very good spatial resolution observed (2.3 nm), we were able to locate those doping sites.

1 A. G. Milekhin, M. Rahaman, E. E. Rodyakina, A. V. Latyshev, V. M. Dzhaganc and D. R. T. Zahn, Nanoscale, 2018, 10, 2755–2763.

Naomi Halas enquired: Do theorists have any suggestions about what experimentalists should be measuring?

Javier Aizpurua responded: The experimental effort to identify the role of plasmon-induced hot electron chemistry is tremendous and extremely useful, so far. In the same way that theory lacks an entire compact methodology to address the whole dynamical process including hot electron generation in a large nanoparticle, and later injection in a particular adsorbate (mainly due to the multiscale nature of the problem both in time and space), I also have the feeling that it might be good to experimentally try to access the dynamics of chemical reactions more in situ and in real time. Couldn't we try to combine ultrafast techniques which could provide some information on the dynamics of both aspects of the problem? We could use linear optical absorption and scattering techniques, as we do nowadays, together with other condensed-matter techniques such as photoemission spectroscopy (PES), or scanning-tunneling microscopy (STM)-induced fluorescence and Raman scattering. And all this could be merged with pump and probe techniques. Of course these techniques address more academic situations, and might be far from the real world of interesting chemical reactions in more realistic situations, but it might be interesting to identify good testing situations, and to merge efforts from the chemistry community, the ultrafast optics community and the condensed matter community. I realize that this is not trivial at all, and at least as challenging as the theoretical efforts needed, or even more.

Alexander Govorov commented: For the rates and efficiencies of generation of nonthermal high-energy (hot) electrons, both size and shape are important. In nanocrystals of small sizes, one should expect higher efficiencies of hot electrons generated via the surface-scattering mechanism, since the surface-to-volume ratio is larger. Also, the shape of a nanocrystal matters since it determines the position and strength of the plasmonic resonance and also an intensity of the electric fields inside a nanocrystal; this internal electric field generates hot electrons near the surfaces where the electron momentum is not conserved. Plasmonic nanocrystals with complex shapes and hot spots are good generators of hot electrons. Some examples are nanostars and nanostructures with narrow plasmonic gaps (a nanocrystal near a mirror and a nanoparticle dimer).

Jeremy Baumberg addressed Alexandra Boltasseva: In your plasmonic enhanced systems you need to use very thin layers of photocatalytic materials – whose properties are different to bulk. Do you see more photodegradation when you make them this thin (we have seen this in many systems)? How are the properties changed by the additional quantum confinement effects, or increased

surfaces which change the film reconstructions and strain? Are there ways to characterise these without TEM (which only looks at a tiny fraction of the film)?

Alexandra Boltasseva answered: No, we did not see any degradation in our hematite films. Indeed, one of the strengths of hematite is its high stability under PEC conditions. We tried only ~15nm hematite thickness where we have not studied any quantum confinement effects. Going to 2D hematite might provide unique properties that could be enhanced/modified by interaction with surface plasmons. See for example ref. 1.

1 A. Puthirath Balan, S. Radhakrishnan, C. F. Woellner, S. K. Sinha, L. Deng, C. L. Reyes, B. M. Rao, M. Paulose, R. Neupane, A. Apte, V. Kochat, R. Vajtai, A. R. Harutyunyan, C. W. Chu, G. Costin, D. S. Galvao, A. A. Martí, P. A. van Aken, O. K. Varghese, C. S. Tiwary, A. Malie Madom Ramaswamy Iyer, P. M. Ajayan, Nat. Nanotechnol., 2018, 13, 602–609.

Junyang Huang commented: The efficiency of the solid-state configuration used here for water splitting is, to some degree, limited by the fact that water molecules are not able to freely move into the plasmonic hotspot. However, if the equivalent system could be constructed in the colloidal suspension (i.e. making many small divisions of reactors which are stable in the aqueous phase), do you think the accessibility of the hotspot and surface to volume ratio could be significantly improved and therefore enhance the efficiency of the system? What are the major challenges associated with transforming catalysis into the colloidal system?

Alexandra Boltasseva replied: Photoelectrochemical systems based on thin films and colloidal suspensions of nanostructures are two different technological approaches in photocatalysis. In general, the former enables a higher solar-to-hydrogen (STH) efficiency (i.e. the current benchmark is around 20%), while the latter provides a much lower STH efficiency, with the current benchmark being around 1% for a solar water splitting colloidal catalyst. Besides, the major challenges associated with using a colloidal system are related to oxygen/hydrogen separation, catalyst recyclability and recovery. Most of all, in colloidal systems it is very challenging to achieve a high charge carrier lifetime and spatial separation, which strongly limits the overall efficiency. Otherwise, PEC systems allow us to separate energetics and kinetics constraints by using two electrodes to drive oxygen and hydrogen evolution, respectively, with the additional benefit of applying a bias to control the water splitting process. We think that for some chemical reactions the colloidal approach is more convenient in terms of hot spot configuration, and the use of hot carriers can be more convenient than in thin films.

Emiliano Cortes asked: The idea of semi-metals as alternative materials for plasmonic applications sounds interesting. However, our control on patterning/colloidal synthesis for traditional plasmonic metals is highly advanced compared to that for semi-metals. What is the state-of-the-art and the challenges for patterning or nanostructuring semi-metals?

Alexandra Boltasseva responded: Significant progress has been reported in the literature regarding the nano-patterning of semi-metals like titanium nitride and zirconium nitride. Titanium nitride is also compatible with standard CMOS processes. See for example, Li et al.1 and Chaudhuri et al.2

1 W. Li, U. Guler, N. Kinsey, G. V. Naik, A. Boltasseva, J. Guan, V. M. Shalaev and A. V. Kildishev, Adv. Mater., 2014, 26, 7959–7965.

2 K. Chaudhuri, A. Shaltout, D. Shah, U. Guler, A. Dutta, V. M. Shalaev and A. Boltasseva, ACS Photonics, 2019, 6, 99–106.

Jeremy Baumberg opened a general discussion of the paper by Stephen B. Cronin: I am puzzled by your data on the grating reflectivity and photocurrent vs. angle in Fig. 4 in your paper. They are not the same – the peaks are shifted, and of different widths. Is it obvious why this is? I suggest this tells us something about where the photocatalytic activity is going on – where on the profile the photocatalysis is happening. You can calculate back from the photocurrent to the near-field generation position, and thus localise where is most active. I wonder if on the sloping edges of the deposition that there are more step-edges and higher roughness creating improved photocatalysis? Can you measure this with STM/AFM?

Stephen B. Cronin answered: This is indeed a puzzling phenomenon, however, one that we observe consistently over repeated measurements with different samples. I think it is unlikely that roughness varies much along the period of the grating. And, while it is likely that the photocurrent is produced predominately in the high field region of the grating (see Fig. 5c in our paper), and thus not produced uniformly over the grating surface, I don't think this will result in a shift in or broadening of the resonant angle, since the periodicity is still the same. It is worth pointing out that photoreflection is an instantaneous process, whereas the hot electron injection is finite. As such, there can be other mechanisms of damping in the system that lead to these shifts and increased broadening of the peaks.

Yonatan Sivan asked: Among other things, you showed the change in transmissivity of a metal grating under optical illumination by a strong pump. Can you give us a historical perspective please by comparing to the numerous earlier studies of the same configuration (e.g., by the van Driel group, the Vallee group, and many others)?

Stephen B. Cronin replied: Work from the van Driel group1 is probably most closely related. Here, ultrafast control of grating-assisted light coupling to surface plasmons was explored, in which 810 nm pulses produced a shift of the 570 nm plasmon resonance by ~0.75 nm with a reflectivity change up to 6% and decay time of ~1 ps. These DR/R spectra show similar profiles which have a positive and negative component, centered around the plasmon resonance. Vallee's group2 has measured the ultrafast nonlinear response of metal nanoparticles and nanorods to be of the order of 1-2 ps. These data are understood on the basis of a model describing the wavelength and time-dependent

modifications of the object material dielectric function. Perhaps most recently, Planken's group3 looked at the effect of metallic bilayers on the ultra-fast dynamics of grating structures, and found that the presence of a buried dissimilar metal layer strongly affects these relaxation times. While the general relaxation time of these transient absorption features is consistent with our results (~1-2 ps), what hasn't been reported before in these time-resolved studies are distinctive features associated with resonant and non-resonant excitation presented here.

1 N. Rotenberg, M. Betz and H. M. van Driel, Opt. Lett., 2008, 33, 2137-2139.

2 T. Stoll, P. Maioli, A. Crut, N. Del Fatti and F Vallée, Eur. Phys. J. B, 2014, 87, 260–278.

3 S. Edward, A. Antoncecchi, H. Zhang, H. Sielcken, S Witte and P. C. M. Planken, Opt. Express, 2018, 26, 23380–23396.

Niclas Sven Mueller enquired: Do you have an explanation why interband transitions cause a positive signal in the transient absorption spectra? This would imply that the absorption probability by interband transitions increases upon illumination by a pump pulse.

Stephen B. Cronin responded: Upon pump excitation (560 nm), 6s band electrons are excited to empty states above the Fermi level, creating an electron-hole population in the 6s band around the Fermi level. The absorption peak around 520 nm corresponds to the transition from the filled 5d band to holes in the 6s band, therefore the transient signal is positive on the spectrum. A slight decrease in the signal should be expected at higher energy probes due to blocking of absorption by electrons above the Fermi level. In our experiments with other pump wavelengths (680 nm, for example) that reduction in absorption is observed at higher probe energies. However, for the 560 nm pump, the reduction in absorption due to electrons above the Fermi level is small. Further studies are needed in order to obtain a complete understanding of these subtleties.

Andrea Marini noted: Your paper nicely reports a hot electron-driven transient absorption spectroscopy in plasmon resonant grating structures. Such a nonlinear process has already been reported before in the reflection by thin films and in propagating surface plasmon polaritons in gold nanowires. However, in such previous investigations, the surface plasmon resonance was playing a minor role and the reflectance/transmission modulation arises from the Fermi smearing of conduction electrons that modulate metallic absorption and dispersion. Can you please comment on the role of the surface plasmon resonance in your experimental findings? Does the reflectance modulation arise from a nonlinear shift of the plasmon resonance itself?

Stephen B. Cronin answered: The transient absorption signal of the surface plasmon resonance is the result of the "Fermi smearing" phenomenon. In detail, upon pump excitation, electrons in the 6sp band are excited to the empty state above Fermi level. The instantaneous excitation by the pump

will result in a non-Fermi–Dirac distribution around the Fermi level. After a short relaxation time, about 50 fs, a new "hotter" Fermi–Dirac distribution is formed through electron-electron scattering. Then the energy will dissipate to the metal lattice through electron–phonon scattering and phonon–phonon scattering, of which the lifetime is greater than 100 ps. The surface plasmon oscillation frequency is a function of the density of electrons in the metal and the mean free path of electrons in the Drude free electron model. "Fermi smearing" upon pump excitation will result in a hot Fermi–Dirac electron distribution. This will lead to higher average kinetic energy. According to the Bohm Gross electron dispersion equation, increasing thermal energy of electrons results in a higher plasmon resonance frequency and the absorption is broadened. In the spectrum, the transient absorption signal appears to be a large depletion and two wings on the sides, which is a result from subtracting the broadened transient signal from steady state plasmon resonance absorption.

Madasamy Thangamuthu remarked: The photocurrent shown is difficult to understand. Is the photocurrent generation due to the electron transfer or hole transfer? If your answer is due to the electron transfer, then is it photoanodic (electrons injected into the back metal contact) or photocathodic (electrons injected into the electrolyte solution)?

Stephen B. Cronin replied: We observe AC photocurrent under both oxidation (positive electrode potentials) and reduction (negative electrode potentials) conditions. For oxidation, the charge transfer process can be thought of as an electron transferred out of the adsorbed molecule into the hole state in the metal electrode. For reduction, the charge transfer can occur as an electron being injected into a reactant adsorbed on the surface of the electrode or directly into the electrolyte solution. However, the barrier for producing a solvated electron is most likely too high to contribute significantly to the observed photocurrent.

Naomi Halas questioned: The spectral structure is really quite different for one polarity compared to the other – do you have any insight on how this relates to the DOS?

Stephen B. Cronin responded: The spectral structure difference comes from whether electronic surface plasmons are excited. Electronic surface plasmons are excited when the probe is in p-polarization with respect to the grating, while they cannot be excited when the probe is in s-polarization to the grating. Other theoretical studies have reported on the density of states of Au.1 The electronic density of states of gold can be described as being composed of a broad and diffuse 6s-p band spanning the Fermi level, and a 5d band with a larger density of states several eV below the Fermi level. We think that the pump laser excites electrons from the 6s-p band below the Fermi level to empty states above the Fermi level, generating holes and electrons in the 6s-p bands. Two excited state absorption peaks were observed in the spectra. The peak around 510 nm is the excess absorption corresponding to excitation of 5d electrons to 6s-p holes. The peak around 470nm corresponds to electrons excited from the 5d band to empty states above the Fermi level by the probe. Since the broadness of the depletion and absorption peaks are similar, one can make a rough calculation of how deep the 5d-band is with respect to the Fermi level. In the TA data, the spectra cross zero at around 480 nm, which implies that the 5d band in Au is 2.6 eV below the Fermi level. This finding is consistent with other theoretical DOS studies.2

1 L-M. Yang, M. Dornfeld, T. Frauenheima and E. Ganzb, Phys. Chem. Chem. Phys., 2015,17, 26036–26042.

2 U. Kreibig and M. Vollmer, Optical Properties of Metal Clusters, Springer-Verlag Berlin Heidelberg, 1995.

Zachary Schultz said: Do you see changes in the overpotential at which the reaction, either H+ reduction or O2 evolution, proceeds with the plasmonic catalyst? This should also be affected by the solution pH.

Stephen B. Cronin answered: The electrolyte condition was pH = 7, 0.5M Na2SO4 solution. We haven't yet explored these processes in solutions with different pH values for HER and OER, however, that would be an interesting set of experiments to perform in order to gain a better understanding of any changes in the overpotential of these reactions.

Yuri Diaz Fernandez opened a general discussion of the paper by Laura Fabris: I hope we will all agree that in the field of anisotropic nanoparticles, we commonly address materials as "gold" nanorods or "gold" nanostars, despite the fact that silver may be incorporated to different extents into these materials, depending on the synthetic conditions. Do you have any comment on the effect of silver on the nucleation of TiO2 at the surface of these materials and on the role of silver/gold alloys on the efficiency of hot electron generation in anisotropic nanoparticles?

Laura Fabris replied: This is an excellent point. Currently, the community is starting to become more clear on the actual presence of non-negligible amounts of silver on anisotropic nanoparticles, which originate from the need to employ AgNO3 to induce anisotropy during growth. We have recently shown1 that monolayers of Ag (in addition to the presence of Ag+) can be clearly measured using STEM-EDX, and that the position and characteristics of these monolayers depend on the initial concentrations of AgNO3 used. Clearly, it is possible that Ag will influence the growth of TiO2. While we have not yet studied this effect, we will be looking into it in the near future. As for how the presence of Ag may influence hot electron generation, this will likely not come from differences in LSPR due to the presence of Ag. It will likely be due to Ag atoms inducing strain at the interface or representing defects that are obstacles to electron transfer across the interface.

1 S. Atta, M. Beetz and L. Fabris, Nanoscale, 2019, 11, 2946–2958.

Bhavesh Kumar Dadhich asked: Is it possible to produce hot electrons and photo-thermal effects using a non-coherent light source?

Laura Fabris answered: Yes, indeed these experiments were carried out under illumination of a Xe arc lamp, which is a non-coherent light source.

Bart de Nijs commented: The presented star shape is an out of equilibrium structure for gold nanoparticles. When you heat these structures they will attempt to revert back to a spherical shape. Have you compared absorption spectra before and after the experiments to see if there have been any significant changes to the optical properties of the structures?

Laura Fabris replied: Indeed, nanostars will likely revert into spheres if treated at high temperatures in operando. In fact, an excellent paper from the groups of Bals and Liz-Marzan1 shows, by using TEM tomography with in situ heating, that the shape of gold nanostars is rapidly modified due to atom migration as the temperature is increased. This is why we need to run the TiO2 reaction at 70 degrees. However, TiO2 is likely offering good thermal protection to the particles once they are completely coated. Monitoring the LSPR position after photocatalytic conversion does not show substantial differences leading us to hypothesize that TiO2 represents an excellent barrier against reshaping.

1 H. Vanrompay, E. Bladt, W. Albrecht, A. Béché, M. Zakhozheva, A. Sánchez-Iglesias, L. M. Liz-Marzán and S. Bals, Nanoscale, 2018, 10, 22792–22801.

Bartlomiej Jankiewicz commented: You have mentioned in your article that plasmonic materials with spherical geometry suffer from limited LSPR tunability, which still leaves the majority of the solar spectrum untapped. However, as has been shown by the work of Prof. Halas on spherical core-shell nanostructures you may tune their optical properties in a broad spectral range simply by changing their geometry. You have also mentioned that you are not able to obtain a full shell for Au nanorods, while you are able to do that for Au nanostars. This is likely related to the coating procedures in which you are using an alcohol solvent for stars and water for nanorods. Organic titania precursors undergo fast hydrolysis in the presence of even small amounts of water, which makes the reaction with them quite difficult to control. However, you may try to use less reactive titania precursors such as TBT. Why do you heat your samples for two days at 70 degrees instead of doing that e.g. for a few hours at 90 degrees? Based on the extinction spectra modification of Au nanorods with TiO2 doesn't significantly change their optical properties. Don't you then think that the higher reactivity of the AuNR-TiO2 structures can be related to formation of the interface between semiconductor and metal?

Laura Fabris responded: When I mentioned the limited LSPR tunability in spherical gold nanoparticles I meant solid spherical particles, which differ from Prof. Halas' nanoshells. Nanoshells have a silica core and a gold shell of variable thickness. The relative size of the core vs. the whole nanoparticle and the thickness of the shell are what contributes to the LSPR tunability obtained for these materials.

It is true that we were not able to obtain a full TiO2 shell on nanorods and this is due to the need to synthesize it in a water environment, where the CTAB shell is not compromised as is observed in alcohols, where the critical micelle concentration of CTAB is modified, leading to the "unzipping" of the micelle. As you correctly point out, employing a less reactive precursor will likely improve the properties of the shell. It is not possible to synthesize the shell on nanostars at temperatures higher than 80 degrees, due to the sensitivity of the nanostar spikes to adatom migration, which is high at locations with a high radius of curvature and is further accelerated at higher temperatures. If nanostars are treated above 80 degrees, the sharpness at the tips is severely compromised, leading to shifts in LSPR and reduced field localization and, therefore, hot electron generation.

The optical properties of TiO2-coated nanorods are not significantly altered (in LSPR position) because of the limited coverage by the semiconductor.

What we observed with respect to AuNR reactivity is that there is a compromise between the uniformity of the TiO2 shell and the lack of polymer stabilizer. In order to synthesize the TiO2 shell in the absence of a polymer stabilizer, one needs to run the reaction in water (as described above) leading to a compromised semiconductor shell quality. However, these results confirm the importance of leaving the interface unhindered, to improve electron transfer across it.

Rifat Kamarudheen said: In Fig. 4a of the manuscript where the hydrogen production of three different gold nanorods (with different LSPRs) are compared with respect to time, the hydrogen production for nanorods with 910 and 980 nm LSPRs starts to saturate after 20 min while the hydrogen production of the 870 nm LSPR nanorod is still increasing. How would you explain these different trends?

Laura Fabris answered: This is a good point and to be quite honest we are not sure why this is happening. We have carried out these reactions multiple times obtaining similar results. This will be an interesting point to start exploring in our upcoming experiments.

Madasamy Thangamuthu asked: From the TEM image one can clearly see the phase differences but how do you confirm this is anatase? Can it be a mixture of anatase and rutile together? Could you comment on whether it would be advantageous to have a mixture of anatase and rutile?

Laura Fabris replied: We ran XRD characterization studies where we observed the presence of peaks for both rutile and anatase. Because this synthesis is run at a low temperature, it is likely that both rutile and anatase are present in, most likely, a sea of amorphous phase. However, based on the literature, it appears that the presence of both rutile and anatase leads to improved band alignment with the hydrogen reduction half reaction, thus improving yields of hydrogen. In our previously published study1 we also verified this hypothesis, indeed observing improved yields when both rutile and anatase were present.

1 S. Atta, A. M. Pennington, F. E. Celik and L. Fabris, Chem, 2018, 4, 2140–2153.

Julien Mahin enquired: Did you notice any secondary nucleation of the titanium dioxide or does it all form on the surface of the gold nanostars?

Laura Fabris answered: Yes, we observed, in some instances, the presence of secondary nucleation sites for titania nanoparticles. However, this can be avoided by slightly modifying reaction conditions or by post-synthetic purification.

Javier Aizpurua remarked: It is fascinating to compare nanorods and stars for chemical reactivity, as they are nanoantennas which show different bulk to surface ratios, and thus, they could show very different behavior, in principle. The structures in your paper seem like canonical structures to show the role of hot electrons. I do not know if production of hydrogen is the best experiment to look at – as it shows differences of 10% in performance, according to your paper. Are there better or more suitable reactions in which we could look at the performance of more controlled and different ratios of hot electrons and holes, even if they are more academic? Do you have any plan to study this in future?

Laura Fabris responded: There can indeed be better suited reactions to look into in the future. Since I am not a catalysis expert, I welcome suggestions from the audience on interesting chemical processes to look at. Once these reactions are identified, we can define design rules to address them, in particular as it concerns choosing the ideal semiconductor catalyst and energy level alignments.

Sebastian Schlücker noted: Creating and extracting hot carriers is equally important. One of the key aspects in your presentation was to nicely demonstrate how to obtain surfactant-free anisotropic nanostars (tips). I guess this aspect has been overlooked in colloid-based plasmonic chemistry with respect to efficient hot carrier extraction. Could you please share your opinion on the general role of surface chemistry in this area with us?

Laura Fabris replied: As you point out, surface chemistry has an important role with respect to achieving efficient hot carrier extraction. Our results seem to indicate that a very intimate contact between the metallic surface of the plasmonic nanoparticle and the semiconductor is necessary to obtain hot electron injection in the latter. Our results on nanorods, although not definitive, appear to further confirm this hypothesis. In fact, in our report, we show that the yield of hydrogen in nanorods with imperfect TiO_2 shells is equal to that of nanorods reported in the literature in which a uniform titania shell was grown in the presence of a polymer overcoat between the metal and the semiconductor. Therefore, there is evidence that polymer layers or other reaction intermediates left at the interface are going to dramatically affect the performance of the photocatalytic system.

Jeong Y. Park enquired: In your interpretation, you are assuming that there is a Schottky barrier height between gold and TiO2. Do you have some estimation of the Schottky barrier height formed at the Au–TiO2 interface? How does it change with the shape of the Au nanostructures? How does this affect the catalytic activity? In my opinion, trying local probe measurements such as conductive atomic force microscopy on Au nanostructures on a TiO2 substrate would help to understand the local charge transport properties.

Laura Fabris answered: We have based our experiments on a generally estimated value of 1 eV between the Au Fermi level and titania conduction band. Clearly, this may not be the case at the nanoscale, especially when the morphology of the nanoparticle is highly anisotropic. Indeed, measurements that probe the local properties will be highly beneficial and could shine new light on the process.

Yuri Diaz Fernandez opened a general discussion of the paper by Jeong Y. Park: I am curious about the CoO layers observed in your as-prepared nanoparticles. Did you still observe this lower oxidation state after ozone cleaning? Do you have any evidence of lattice strain due to mismatch between the core lattice and the surface CoO layers?

Jeong Y. Park responded: We measured the XPS of Co before and after UV ozone treatment, as shown in Fig. 4c and Fig. S2 in our paper. We found that there were no significant changes in the chemical states of either the platinum or cobalt oxide surfaces while removing the organic capping molecules using UV–ozone. Therefore, we can conclude that the oxidation states of the Co remain almost the same after UV ozone cleaning. We assume that the lattice strain from mismatch between the core lattice and the surface CoO layers is present. The effect of the lattice strain on the catalytic activity of Co oxide nanoparticles is not clear to us and it would be an interesting subject for a follow-up study.

Phillip Christopher asked: Can you use the catalytic diode approach to estimate adsorption energies of species? Because the current should be proportional to exothermicity, would this be an easy way to measure the adsorption energy of molecules?

Jeong Y. Park replied: The catalytic reaction involves multiple processes including adsorption, desorption of molecules, and chemical rearrangement. Hot electrons measured with catalytic nanodiodes can give clues about the exothermicity of a reaction, but it does not give exclusive information about the adsorption process. Therefore, it is challenging to obtain the adsorption energies of a chemical species with a catalytic diode. However, I would like to note that an earlier approach using a Schottky diode focused on the detection of hot electrons generated during the adsorption of molecules. Using this approach, Gergen et al. obtained a correlation between the hot electron flux and the adsorption energy.1

1 B. Gergen, H. Nienhaus, W. H. Weinberg and E. W. McFarland, Science, 2001, 294, 2521–2523.

Reinhard J. Maurer remarked: In Fig. 5 in your paper, the chemicurrent and TOF for the three systems follow the trend: Co_3O_4 NCs/Pt < Pt < UV-treated Co_3O_4 NCs/Pt. What is your current working hypothesis to explain this trend?

Jeong Y. Park answered: The key claim in this study is that the interface between the Pt and cobalt oxide gives rise to enhanced hot electron generation. We explain this trend with a theoretical DFT calculation that shows a lower activation barrier forming for *OH formation at the Pt–cobalt oxide interface1 and a higher exothermicity, which are responsible for the higher catalytic activity and the higher chemicurrent yield, respectively. The effect of UV treatment is to remove the capping layers that were present on the oxide nanoparticles.2,3 Before UV treatment, this capping layer blocks the reactive sites and stops hot electron transport.

1 H. Lee, J. Lim, C. Lee, S. Back, K. An, J. W. Shin, R. Ryoo, Y. Jung and J. Y. Park, Nat. Commun., 2018, 9, 2235.

2 J. Y. Park, C. Aliaga, J. R. Renzas, H. Lee and G. A. Somorjai, Catal. Lett., 2009, 129, 1-6.

3 J. K. Nørskov, T. Bligaard, J. Rossmeisl and C. H. Christensen, Nat. Chem., 2009, 1, 37–46.

Naomi Halas commented: HER and water splitting have been around for a long time. If we took all the money that was ever spent on research into that and split it into all of us in the room we could fund our research for our career. Can we ever solve HER – what are the breakthroughs we need? Should we be looking at other avenues?

Stephen B. Cronin replied: Water splitting is a nice test reaction for developing better understanding of photocatalytic processes in general and developing appropriate materials for these processes. There are still many aspects of these photocatalytic processes that are poorly understood, and it is likely that, ultimately, the “payoff” of this large body of work will be in another reaction or liquid–solid interfacial system.

Phillip Christopher contributed: A lot of technoeconomic analyses have been done that suggest that at the largest scales it will be tough for water splitting to compete with steam methane reforming (SMR), even with close to theoretical efficiencies. Probably the use of water splitting for H_2 generation will be used mostly on small scales, where some advantages exist over SMR, unless significant carbon taxes are levied.

Zachary Schultz questioned: Should we be looking at the materials for other reactions? There have been a lot of comments and reports showing that the chemistry changes what the catalysts are useful for. Can we develop guiding principles based on fundamentals of various reactions to help guide the development of future catalysts?

Jeong Y. Park responded: In our study of hydrogen oxidation, we have used the most well-known (i.e., Pt-based) catalysts. Because noble metals like Pt are quite expensive, there are numerous approaches to develop novel catalysts that are cost-effective and highly reactive. I think an important area is bimetal catalysts because of the potential for improving catalytic performance and reducing cost. I think a theoretical approach can provide additional insight to guide the development of future catalysts.1

1 J. K. Nørskov, T. Bligaard, J. Rossmeisl and C. H. Christensen, Nat. Chem., 2009, 1, 37–46.

Sebastian Schlücker remarked: Guiding principles for this are of course very important yet probably very challenging to obtain. In my opinion we need support from theory which is capable of describing the involved potential energy surfaces (the ground state but also the relevant excited states) as this changes from system to system (metal plus molecule). If possible at all, I expect this type of theory input therefore more likely to come from the quantum chemistry/surface science community than from the plasmonics field.

Naomi Halas noted: Absolutely, that is the future of this field. Looking at what reactors have binding affinities for reactants of interest is a start, and also, with the help of accurate calculations, determining the binding energy for bond dissociation is typically one way of utilizing the antenna particle, that is, tuning its plasmon to or near the energy of bond dissociation of an adsorbate molecule. The reactions should dictate all these specifics.

Conflicts of interest

There are no conflicts to declare.